ONE YEAR PROJECT REPORT

PREPARATION AND CHARACTERIZATION OF CARBON NANOTUBES BARIUM TITANATE COMPOSITES

By

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Under the Supervision
Of

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CERTIFICATE

This is to certify that, the work in the report entitled **"PREPARATION AND** CHARACTERIZATION **OF CARBON NANOTUBES BARIUM TITANATE COMPOSITES"** by **Jyoti Prakash Sahu,** in partial fulfillment of Master of Science degree in **PHYSICS** at the National Institute of Technology, Rourkela (Deemed University); is an authentic work carried out by him under my supervision and guidance. The work is satisfactory to the best my knowledge.

Dr. Pitamber Mahanandia

Date- 10-05-2013 **Department of Physics**

Place- Rourkela **NIT, Rourkela**

DECLARATION

I hereby declare that the project work entitled **"Preparation and Characterization of Carbon Nanotubes Barium Titanate Composites"** submitted to the NIT, Rourkela, is a record of an original work done by me under the guidance of **Dr. Pitamber Mahanandia**, Faculty Member Department of Physics, NIT, Rourkela. This project work has not been performed on the basis for the award of any Degree or diploma/ associate ship/fellowship and similar project if any.

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ABSTRACT

In these paper carbon nanotubes (CNTs)/barium titanate (BTO) composites have been successfully prepared by physical method. The prepared samples with different CNTs concentrations in BTO have been characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). Temperature dependent resistance measurement shows that decrease in resistance with increasing concentration of CNTs in BTO. It is observed from the SEM images that the presence of CNTs in the composites with varying concentration. The detail investigation about dielectric properties of CNTs contained BTO composites are yet to be investigated.

Keywords: Physical method, BaTiO3, CNTs, nanowires, structural and optical properties.

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CHAPTER-I

INTRODUCTION

1.1 About barium titanate

The chemical formula for barium titanate is $BaTiO_3$ (BTO). As a powder it is white to grey in color and has a perovskite structure. It is soluble in many acids like sulfuric acid, hydrochloric acid and hydrofluoric acid. It does not dissolve in alkalis and water. In the pure form it is an electrical insulator. However, on doping with small amounts of metals, especially Scandium, Yttrium, Neodymium, Samarium etc. it becomes semiconducting and it shows positive temperature coefficient of resistivity (PTCR) properties in the polycrystalline form. At the Curie temperature, BTO undergoes a phase change from tetrahedral to cubic. Single crystals of barium titanate exhibit negative temperature coefficient of resistivity (NTCR). $BaTiO_3$ also exhibits ferroelectric properties and is an excellent photorefractive material. Due to its PTCR properties, it is often found to be used as a thermo resistor e.g. in thermal switches. It belongs to the perovskite family having the ABO_3 type structure where 'A' and 'B' represent the cation elements.

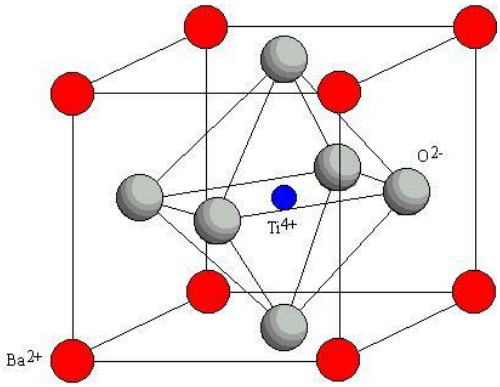


Fig. 1: Schematic diagram of perovskite (ABO_3) type structure.

1.2 Ferroelectricity

Ferroelectricity was first discovered in Rochelle salt (sodium potassium tartarate tetrahydrate) in the year 1921. Ferroelectricity is the property of materials which possess a spontaneous polarization that can be reversed by the application of an external electric field. Due to their unusually high and unusually temperature dependent values of the dielectric constant, the piezoelectric effect, the pyroelectric effect, and electro-optical effects, including optical frequency doubling, ferroelectrics are of theoretical and practical interest. These ferroelectric materials have a wide range of applications in various fields like ultrasonic transducers, high dielectric constant capacitors, radio and communication filters, medical diagnostic transducers, stereo tweeters, buzzers, ultrasonic motors, thin film capacitors, thin film ferroelectric memory storage devices etc.

1.3 Nanoscience and Nanotechnology

There are seven things about nanoscience and nanotechnology which we should know. These are as follow:

1. The concept
2. Definition and usage of the term nanotechnology
3. What's so special about nanotechnology and why is it an issue now?
4. New materials- the rise of carbon
5. Nanomanufacturing
6. The risk factor
7. Social aspects

1.4 Nanotechnology

Nanotechnology is the technology that is conducted at the nanoscale, which is about 1 to 100 nm. Nanoscience and nanotechnology are the study and application of extremely small things and can be used across all the other science fields.

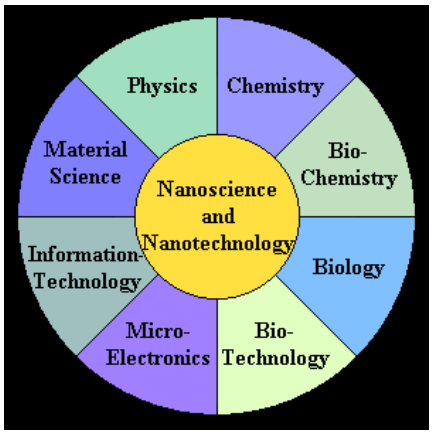


Fig.2: Different fields of Nanoscience and Nanotechnology.

The ideas and concepts behind nanoscience and nanotechnology started with a talk entitled "There's Plenty of Room at the Bottom" by physicist Richard Feynman at the California Institute of Technology (CalTech) on December 29, 1959. Over a decade later, in his explorations of ultra-precision machining, Professor Norio Taniguchi coined the term nanotechnology.

1.5 Properties of nanomaterials

Nanostructure materials are single phase or multiphase polycrystalline solids with a typical average size of a few nanometers (1nm = 10-9m).Basically, the range from (1-100)nm is taken as nano-range for convention as per National Nanotechnology Initiative in the US., and the size of hydrogen atom is considered as the lower limit of nano where as upper limit is arbitrary. The grain sizes are so small; a significant volume fraction of the atoms resides in grain boundaries. Material is characterized by a large number of interfaces in which the atomic arrangements are different from those of crystal lattice. The basic classification of nonmaterial is done based on the confinement. Bulk structures show no confinement whereas nano-wells and nanowires can be obtained by 2-D and 1-D confinement respectively. The quantum realm comes to the picture

when there is a 3D confinement and leads to zero dimension quantum structures that is quantum dot.

1.6 Processing methods

The synthesis of nanomaterial can be well accomplished by two approaches. Firstly, by “Bottom Up” method where small building blocks are produced and assembled into bigger structures. Where the main monitoring parameters are morphology, crystallinity, particle size, and chemical composition.Examples: chemical synthesis, laser trapping, formation of self-assembly, aggregation of the colloids, etc. and secondly, by “Top Down” method where large objects are modified to give reduced features. For example: deposition of films and their growth, nano imprint /lithography, etching method, mechanical polishing etc. the main reason of alteration in various mechanical, thermal and other property arises due to an increase in surface to volume ratio. Synthesis of nanomaterial is most commonly done based on three strategies i.e.

- Liquid-phase synthesis.
- Gas-phase synthesis.
- Vapour-phase synthesis.

a) Liquid-phase synthesis

The techniques used for synthesis are:

1. Co-precipitation.
2. Sol-gel Processing.
3. Micro-emulsions.
4. Hydrothermal/Solvo-thermal Synthesis.
5. Microwave Synthesis.
6. Sono-chemical Synthesis.
7. Template Synthesis.

b) Gas-Phase Synthesis

Super saturation achieved by vaporizing material into a background gas, then cooling the gas.

c) Methods using solid precursors

1. Inert Gas Condensation
2. Pulsed Laser Ablation
3. Spark Discharge Generation
4. Ion Sputtering

d) Methods using liquid or vapour precursors

1. Chemical Vapour Synthesis
2. Spray Pyrolysis
3. Laser Pyrolysis/ Photochemical Synthesis
4. Thermal Plasma Synthesis
5. Flame Synthesis
6. Flame Spray Pyrolysis
7. Low-Temperature Reactive Synthesis

Nanostructured materials can have significantly dissimilar properties, based on the chosen fabrication route. Each method offers some advantages over other techniques while suffering limitation from the others.

1.7 Applications

1. Very high tensile strength
2. Replacement of nanotubes for cheapness in some applications: composite materials and batteries for improved conductivity

3. Hydrogen storage
4. Graphene based quantum computation? Low spin-orbit coupling-> grapheme may be ideal as a q-bit.
5. Transistor applications

1.8 Carbon Nanotube (CNT)

Carbon is the fourth most abundant element on earth. Carbon is an element that exists in four different dimensions. They are diamond (3D), graphene (2D), carbon nanotubes (1D) and fullerenes (0D) whose structural properties are interesting. Among them one dimensional carbon nanotubes shows excellent electrical, mechanical and thermal properties. CNT is a tubular form of carbon with diameter as small as 1nm. Its length varies from few nm to µm. The configuration of CNT is equivalent to a two dimensional graphene sheet rolled into a tube.

Their high mechanical (break strengths reported as high as 200 GPa, and elastic moduli in the 1Tpa), electrical current capacity (10^5-10^8 S/m), thermal properties (1750-5800 W/mK) and high aspect ratio of CNTs make them ideal candidates as fillers to enhance the properties of composites. Techniques have been developed to produce nanotubes in sizeable quantities, including, arc discharge, laser ablation, high-pressure carbon monoxide (CO) disproportionation (HiPco) and chemical vapor deposition (CVD. CVD growth of CNTs can occur in vacuum or at atmospheric pressure.

CHAPTER-II

AIM OF THE PROJECT

The main objective of this project work is to prepare and characterize carbon nanotubes barium titanate composites having various concentrations of carbon nanotubes. By introducing the conducting filler in insulating ferroelectric barium titanate, a composite will be prepared. The aim of this project is to investigate the electrical properties of the CNTs based BTO composites. It is believed that the properties of host matrix BTO will drastically change due to the presence of conducting filler CNTs. In order to prepare CNTs/BTO composite CNTs and BTO are required. The specific objectives are as follows:

1. Preparation of BTO pallet.
2. Preparation of three samples with three different concentrations of CNTs compared with 150 mg of BTO by physical method.
3. To analyse the XRD patterns of the CNTs/BTO composites.
4. Characterize the surface morphology of the CNTs/BTO composites by Scanning Electron Microscopy.
5. Study the electrical properties by R-T measurement.

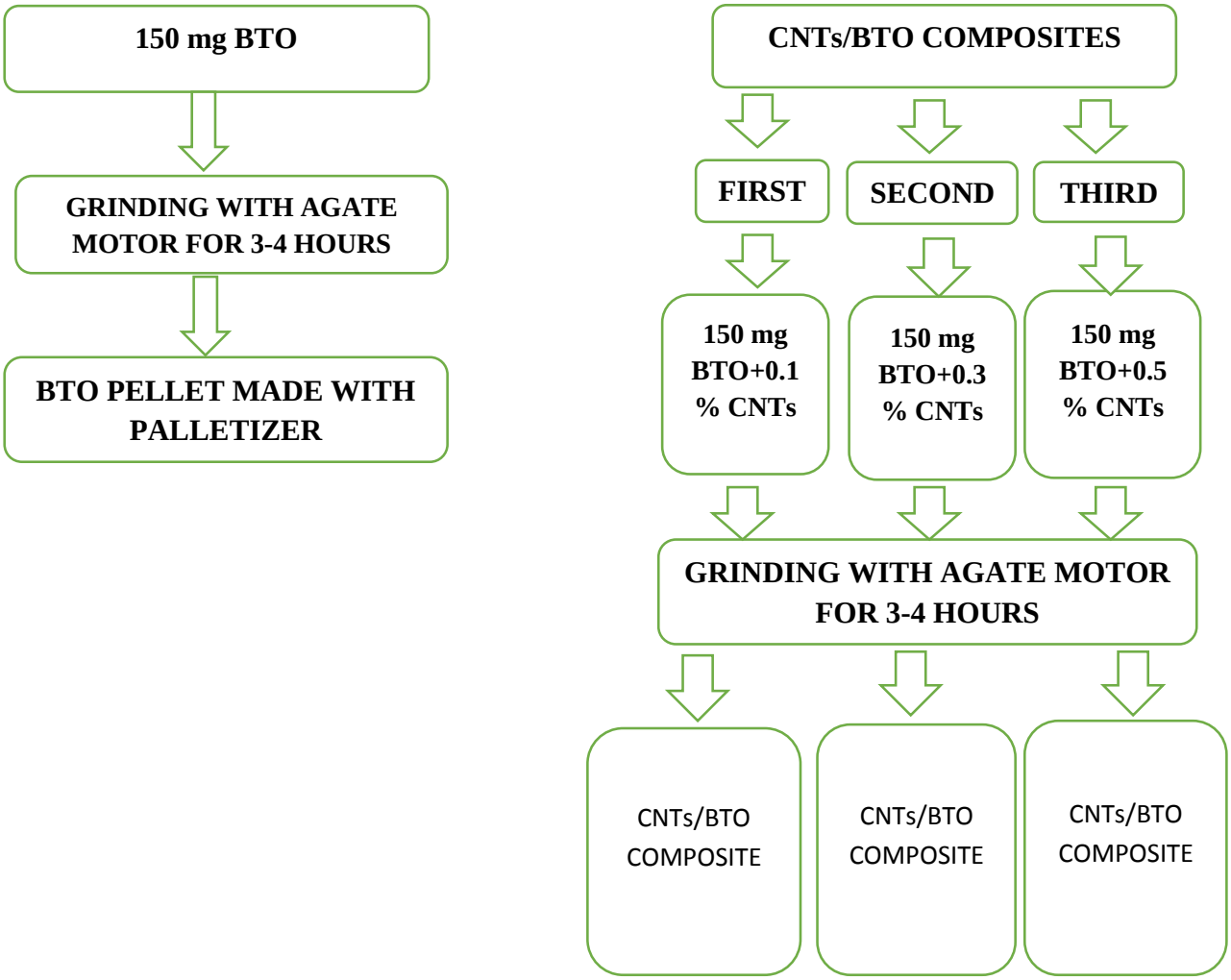
CHAPTER-III

EXPERIMENTAL PROCEDURE

3.1 Preparation of CNTs/BTO composite in physical method

The samples were prepared by physical method (grinding with agate motor). Each sample was grinded for 3-4 hours and with the help of palletizer all samples were prepared. The precursors used in the synthesis of CNTs/BTO composites are barium titanate and carbon nanotubes having purity 99%. In this project work four samples were prepared. Firstly, only one BTO pallet was prepared by taking 150mg of barium titanate with the help of pelletizer and agate motor after grinding for 3-4 hours. This pallet was characterized by SEM. Secondly, 0.1%, 0.3% and 0.5% of carbon nanotubes compared with 150 mg of barium titanate were measured using electronic measuring machine correct up to 4 decimal places. After this three concentrations of BTO each having 150mg were also measured followed by the same machine. In the measured 150mg of BTO material the three concentrations of CNTs (0.1%, 0.3% and 0.5%) were mixed. Then with the help of agate motor each mixed concentration was grinded for 3-4 hours. After that, the powder was taken and shaped in the form of pallets by uniaxially pressing with the help of palletizer for 2 minutes at a pressure of 6 atmospheres. The resulting powders were characterized by various characterization techniques like XRD and SEM. The pallets were characterized by R-T measurement. Necessary graphs were plotted using the x'pert highscore and origin software. The values measured from both the synthesis routes were compared and analyzed.

3.2 Flow chart of sample preparation



CHAPTER-IV

CHARACTERISATION TECHNIQUES

4.1 X-Ray Diffraction (XRD)

XRD is an analytical and most common technique for the study of crystal structure and atomic spacing. It is also used for the identification of phase of a crystalline material and also provides information on unit cell dimensions. It is based on the principle of interference. X-ray diffraction occurs when there is a constructive interference between the monochromatic x-rays and the crystalline sample. X-rays to be used are generated by a cathode ray tube by heating a filament to produce electrons. These electrons are then accelerated with the help of an applied voltage towards the target material and are bombarded with the sample. Constructive interference is observed on the interaction of the electron beam with sample along with the production of a diffracted beam. When the wavelength of the incident X-ray matches with the lattice spacing of the target material according to the Bragg's law of diffraction constructive interference occurs and a peak is observed in the intensity.

According to Bragg's law:

$$n\lambda = 2d \sin\theta$$

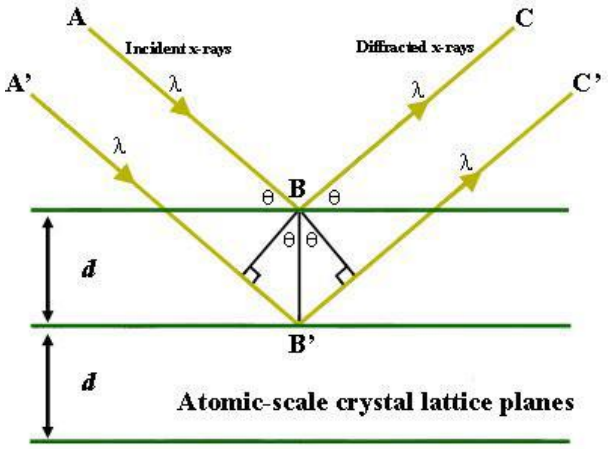


Fig.3 Bragg's diffraction

The intensity of the reflected x-rays is recorded by rotating the sample and the detector. In the present work XRD was done using Philips analytical XRD machine with the wavelength of K-radiation = 1.5418 Å.

4.2 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is used to study the microstructure and topographies of the sample. It scans the surface of the sample to build a 3-D image of the specimen with the help of a beam of electrons. A typical SEM can magnify up to nanometre scale. The basic principle of SEM involves the interaction of the electron beam generated from x-ray tube and the sample surface. This interaction generates a diversity of signals. These signals comprise of secondary electron, backscattered electron, X-rays, photons, heat and even transmitted electrons. Backscattered electrons and secondary electrons are used for the imaging of the sample. Secondary electrons are used to study the topography and morphology of the sample whereas the back scattered electrons help to illustrate the contrast in the composition of multiphase samples. SEM most commonly comes in conjunction with EDAX.

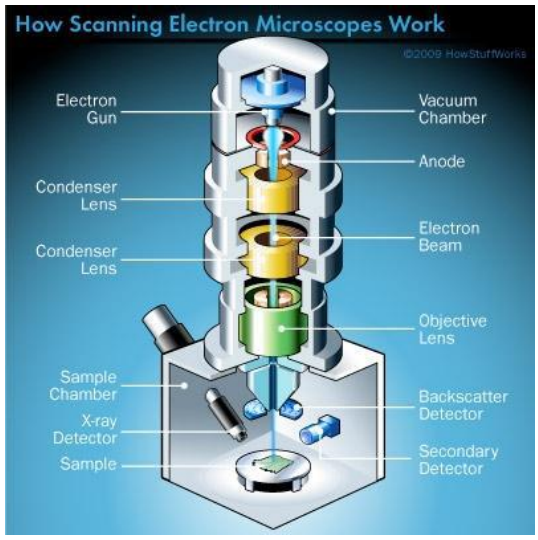
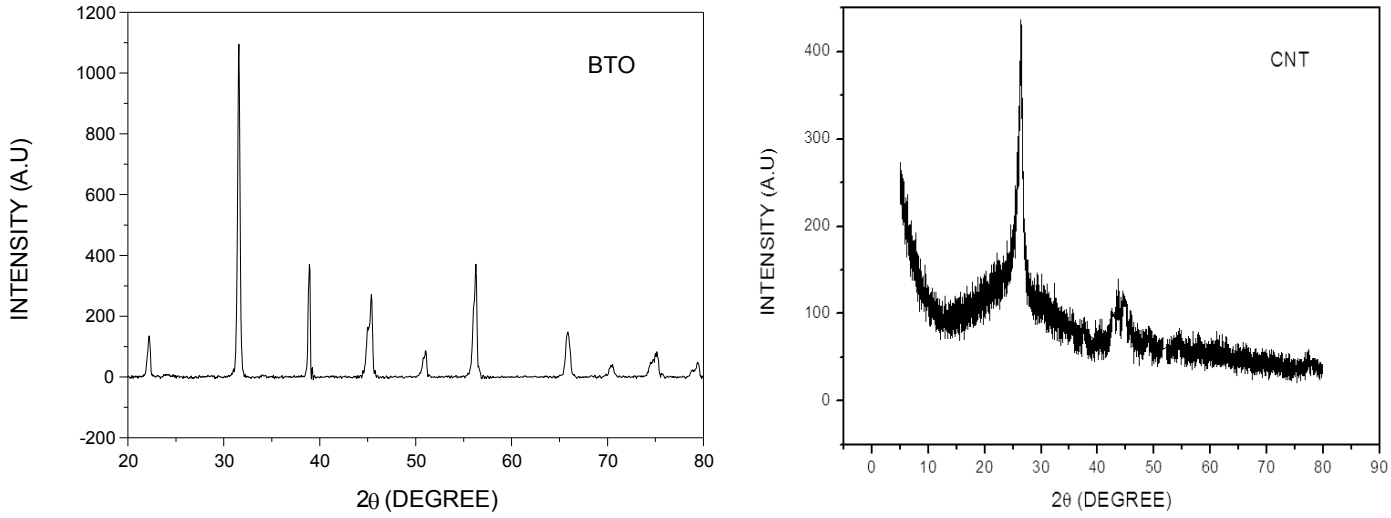


Fig.4: Schematic diagram of a scanning electron microscope (SEM)

CHAPTER-V

EXPERIMENTAL RESULTS AND DISCUSSION

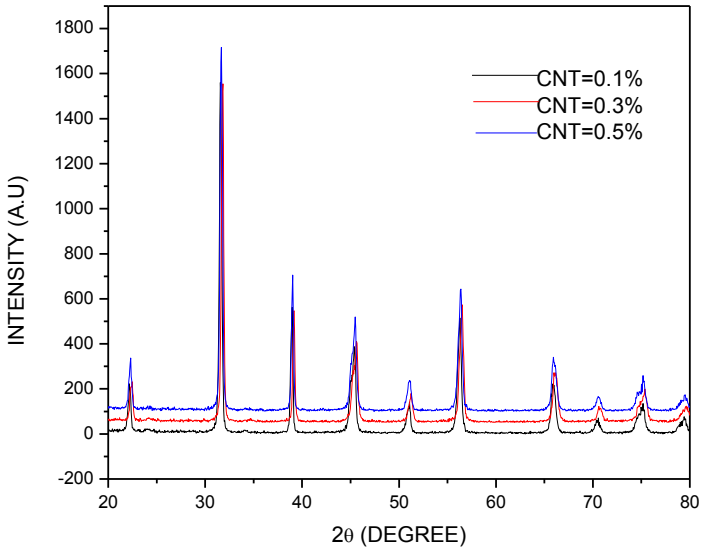
5.1 X-ray diffraction analysis



(a) **(b)**

Fig.5: (a) X-ray diffraction of BTO, (b) X-ray diffraction of CNTs (commercial).

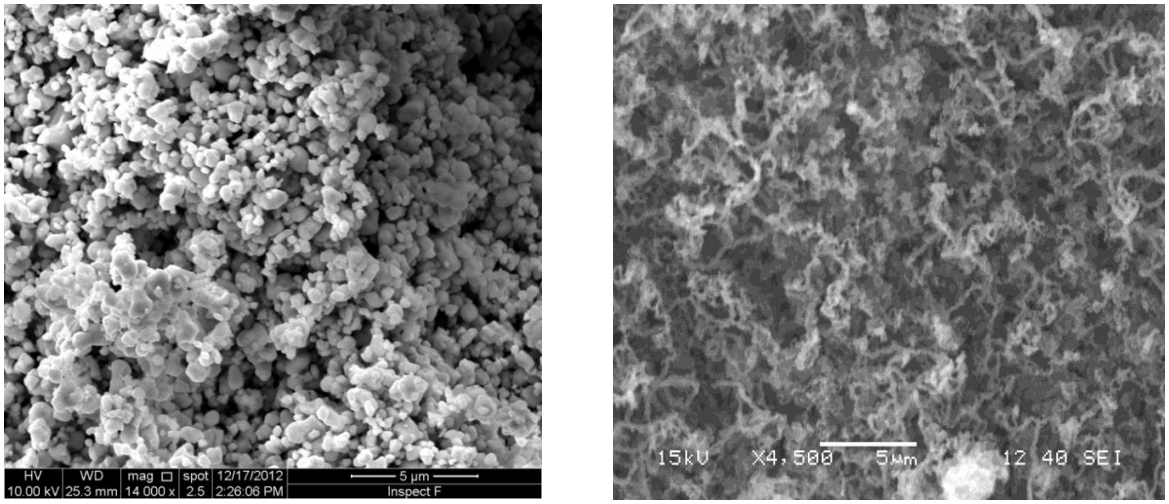
In fig.5 two X-ray diffraction patterns are shown. Fig.5 (a) showing XRD patterns for BTO and fig.5 (b) for CNTs (commercial). Fig.5 (a) has shown highly crystalline single phase material while fig.5 (b) has shown amorphous nature without any secondary/impurity phases. In the XRD plot the peak positions from $2\theta=30^0$ to 40^0 and $2\theta=60^0$ to 70^0 indexed to the cubic structured, which is in good agreement with the reported data (JCP2.2CAa:31-0174). Other diffraction peaks are well consistent with hexagonal phase, which had been confirmed by literature (JCP2.2CA:34-0129). CNTs have a graphitic peak at $2\theta=26^0$.



(c)

From fig.5 (c) it has been observed that the graphitic peak is suppressed and the reason is yet to be obtained. This may be due to dominant of BTO on CNTs due to its higher concentration.

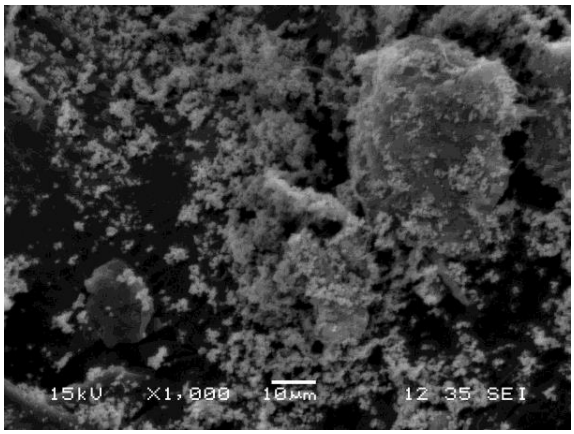
5.2 SEM images



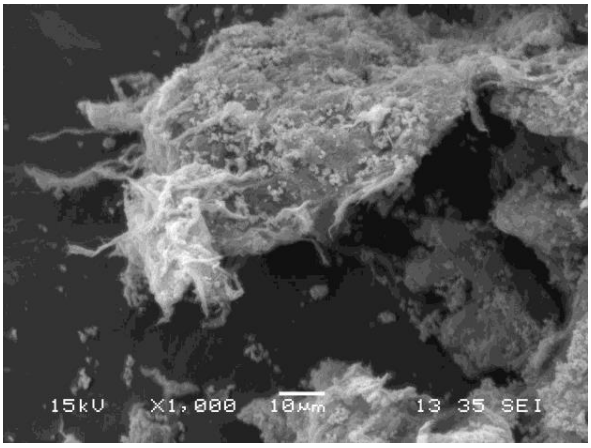
(a) BTO **(b) CNTs (purchased MWCNTs)**

Fig.6: Scanning electron microscopy images

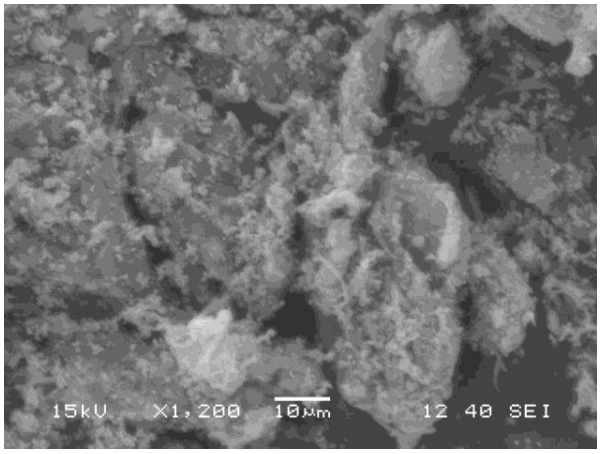
The above figure showing the SEM images of BTO and CNTs (Purchased - MWCNTs). In fig.6 (a), the grains are granular in shape and are uniformly distributed. Fig.6 (b) has shown the structures of carbon nanotubes.

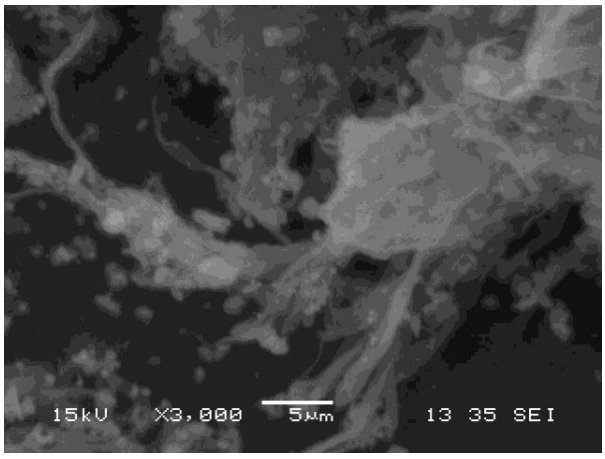


(c) 150 mg BTO+ 0.1% CNTs



(d) 150 mg BTO+ 0.3% CNTs





(e) 150 mg BTO+ 0.5% CNTs

The SEM images in fig.6 (c), (d) and (e) confirm the presence of CNTs with varying density in the prepared CNTs/BTO composites.

5.3 R-T measurement

The resistances of first (0.1 % CNTs), second (0.3 % CNTs) and third (0.5 % CNTs) samples were found to be 209 Ω, 129 Ω and at 58 Ω room temperature. It was confirmed that the resistance of the samples decreasing with increasing CNTs concentration.

CHAPTER-VI

CONCLUSION

CNTs/BTO composites were successfully prepared through physical method by considering different concentrations of CNTs. The XRD results of CNTs/BTO composites showed that the graphitic peaks of the composites are supressed because of higher concentration of BTO however the reason is yet to be ascertained. The SEM images confirm the presence of CNTs with varying density in the prepared composites. From the resistance measurements, it was observed that the resistance decreases with increasing CNTs concentration. Since this work is unique so better analysis will be adopted to study the properties by TEM, Raman spectroscopy and dielectric measurements and these can be achieved by doing ball milling method of the composites.

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